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Influence of the chemical composition on steel casting performance

Roney Eduardo Lino^{a,*}, Ângelo Máximo Fernandes Marins^a, Leandro Aparecido Marchi^a,
Jamyllle Assis Mendes^a, Lucas Vieira Penna^a, Joaquim Gonçalves Costa Neto^a,
João Henrique Palmer Caldeira^a, André Luiz Vasconcellos da Costa e Silva^b

^a ArcelorMittal Monlevade, G. Vargas Ave. 100, João Monlevade, Minas Gerais, MG, Brazil

^b EEMVR-UFF, Trabalhadores Ave. 420, Volta Redonda, Rio de Janeiro, RJ, Brazil

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ABSTRACT

Improving the quality of steel and the steelmaking process has been a matter of routine for metallurgical engineers and steelmaking companies in a demanding market for quality products at highly competitive price. The chemical and temperature adjustment are made during the secondary refining process, as well as the inclusion modification required to product quality, and also the demand for castability accuracy. Continuous casting process is the most used solidification casting process, in which the flow of pouring liquid metal through the submerged entry nozzle is assured by the correct temperature and the formation of liquid inclusion in the casting temperature. Thermocalc and CEQCSI were the software used in this work to assess the effect of carbon, silicon and sulphur in the castability window of the aluminium vs calcium phase diagrams. They have proved to be highly suitable and effective and the results showed that the chemical elements used directly affected the position of the castability window of carbon steel. An analysis of a 0.2%C billet sample using Scanning Electron Microscopy showed that there is a great heterogeneity of inclusions in aluminium-killed and calcium-treated steel.

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1. Introduction

The accurate treatment of steel in ladle for the proper control of deoxidation and inclusions in the products is essential to produce billets from the continuous casting process [1,2]. The formation of liquid inclusion after the secondary refining is considered a precondition for the steady flow of liquid metal through the small diameter nozzles of the continuous

caster. The steel castability is mainly influenced by the formation of solid micro-inclusions into liquid metal, and the inclusion deposition rating in the nozzle is due to the steel cleanliness [3]. The chemical adjustment in the ladle furnace can be very accurate, as well as the desulphurization and calcium-treatment. The addition of the calcium cored wire is able to change the physical characteristics of the inclusions during the deoxidation process. Clearly, the solid-liquid transformation is a function of the liquidus temperature of these

* Corresponding author.

E-mail addresses: roney.lino@arcelormittal.com.br, roneysider@hotmail.com (R.E. Lino).

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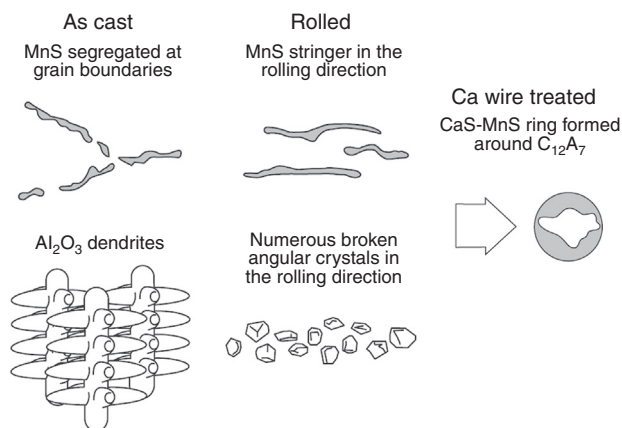


Fig. 1 – Schematic illustration of the modification in the morphology of the inclusion after calcium treatment [8].

inclusions. Inclusion phases at a work temperature can be predicted by calcium vs aluminium phase diagrams, in which the liquid phase defines the area of the diagram called “castability window” [4–6].

The modification of the morphology of the inclusions in steel by calcium treatment not only allows the continuous liquid steel stream during the continuous casting process but also provides an important enhancement of the quality of high-strength alloy steel. For instance, the properties of fatigue strength required in some applications depends directly on the inclusion chemical composition, shape, and distribution of their sizes. Angular, long and hard inclusions must be avoided as they cannot be deformed along with the steel matrix along the hot rolling process, which can result in stress concentration into the interface steel/inclusion [7]. Fig. 1 shows, schematically, how the morphology of the inclusions can be changed by calcium treatment [8]. In this outline, the inclusions in aluminium killed and calcium treated steel are spherical with a low-melting-point calcium aluminate core, covered by calcium and manganese sulphides. The inclusions at relatively-low melting point, smaller in size and spherical are recommended to improve the fatigue strength and toughness properties and also prevent or decrease the hydrogen embrittlement [1,3,7,9,10].

The aim of this study is to assess the influence of the sulphur content and the deoxidant elements, silicon and carbon, in the steel castability window produced by the ladle furnace → continuous caster process.

2. Experimental procedure

Fifty-four steel chemical compositions with different content of carbon (0.2, 0.4 and 0.6%), silicon (0.02 and 0.20%) and sulphur (0.005, 0.010 and 0.015%) were selected corresponding to the industrially produced alloys (e.g. SAE 1020, SAE 1040 and SAE 1060). The liquidus temperatures were calculated by using Thermocalc, a thermodynamic computer software, since it can calculate accurately the liquidus temperature to a wide range of the chemical composition [11].

Calcium vs. aluminium phase diagrams were calculated for the fifty four alloys by the software Thermocalc using SLAG2 database. The diagrams were calculated in function of aluminium and calcium content at 50 °C above the liquidus temperature of the steel. Although they may affect the “castability window”, the total oxygen content and pressure used in the trials were continual at 20 ppm and in 1 atm respectively, and the other chemical elements present in steel were also assumed constant. The effects of these influences will be assessed in future studies.

The minimum and maximum calcium content required to achieve liquid inclusion in function of the aluminium content were identified in these aluminium versus calcium diagrams, and the aimed value was taken as the average between the minimum and maximum values. By using the aimed calcium content from the calculations and the chemical composition of the alloys, a multiple regression was carried out by using the software Minitab.

The casted samples of industrially-produced billets through continuous casting were assessed. The inclusions were analysed by the Scanning Electron Microscopy (SEM), in which the types of oxides present were identified in semi-quantitative analysis. The liquidus temperature and phase fraction of the inclusions were calculated on the basis of chemical composition by the thermodynamic software CEQCSI (Crystal module).

Fig. 2 shows the main screen of the thermodynamic software used in this work.

3. Results and discussion

The aluminium–calcium phase diagrams at 50 °C above the liquidus temperature of the alloys were calculated for all the proposed chemical compositions, keeping the other elements constant, as described above. As known, carbon content

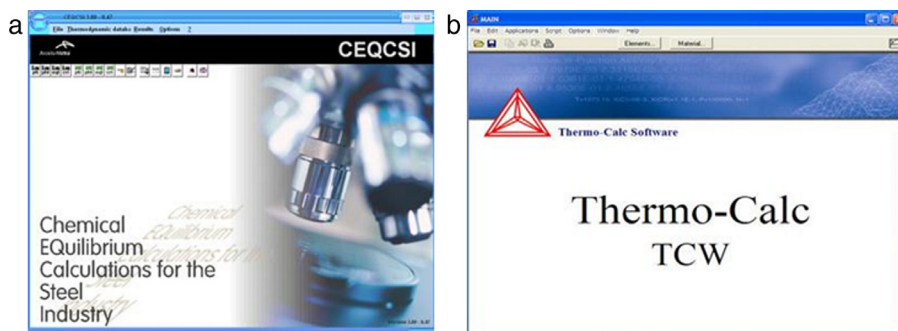


Fig. 2 – Screen of the thermodynamic software (a) CEQCSI (b) Thermocalc.

Table 1 – Average liquidus temperature of the alloys according to carbon content.

Carbon of alloy	Average liquidus temperature calculated
0.2%	1521 °C
0.4%	1504 °C
0.6%	1486 °C

directly influences the steel melting temperature, ranging from 1521 °C in low-carbon steel (0.2%C) to 1486 °C in high-carbon steel, as given in Table 1. The awareness of the liquidus temperature and steel temperature control in the refining and casting processes is essential to ensure the continuity of the productive process at melt shop [7].

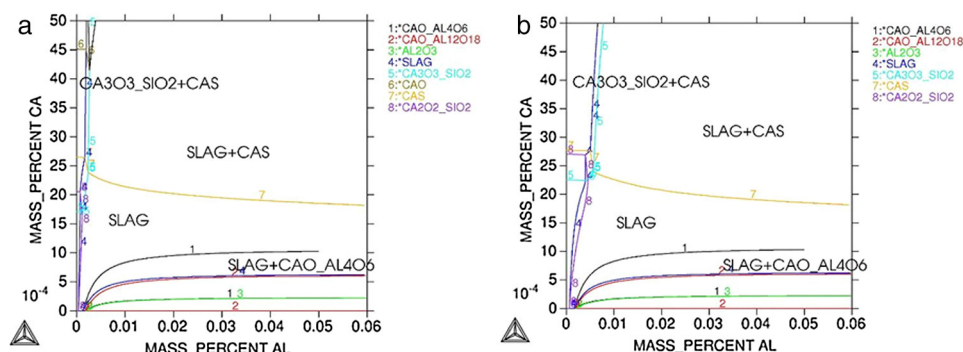
Fig. 3 shows the aluminium vs calcium diagrams for a 0.2%C, 0.05%S and 0.02%Si steel (and 20 ppm O_{total}). In the figure, the solid phases of calcium aluminates, calcium silicates and sulphates are quantified, as well as the formation of liquid inclusions (SLAG) in the simulation temperature. The area quantified in the diagram for such liquid inclusions is of great industrial importance, once it represents the area of the “castability window” [4]. This area, which represents a specific zone of calcium content, must be aimed to ensure a suitable steel castability. The fact that the inclusions in this area are in the liquid state stimulates the spherical shape, which is easier to be removed from steel [7]. Above this area on the left (lower aluminium and higher calcium) the solid phase of calcium silicate is shown. On the right of this area (higher aluminium and calcium content) are the phases of calcium sulphide with liquid inclusion. Below the castability window is the area of solid calcium aluminate with liquid inclusions and just below the area of solid inclusions of calcium aluminate. All the areas with solid phases should be avoided due to the risk of nozzle clogging at the continuous caster [5].

By comparing the results of Fig. 3a of a steel with 0.02%Si with a similar chemistry with silicon content 10 times higher (0.20%), there was a significant difference in the position of the solid phase area of calcium silicate. In higher silicon content steel, this area extends to aluminium content up to 0.008% (Fig. 3b).

Fig. 4 shows the values calculated for calcium content that should be aimed to obtain the liquid phase inclusions at 50 °C above the steel liquidus temperature, i.e., the calcium content required so that the inclusions are kept exactly in the centre of the window castability. The graphs show the

influence of aluminium, sulphur, silicon and carbon in the position of the castability window. It is clear that such chemical elements directly influence the equilibrium between the oxides and sulphides phases present in steel. Aluminium, while an element of greater attraction for oxygen among the elements studied, did not present significant influence on the aimed amount of calcium, regardless of the content of other elements. This is due to the fact that the aluminium variation from 100 to 300 ppm has little influence for the equilibrium of the system. In this case, the aimed calcium content is virtually constant for this aluminium content range, considering the other elements as constant. The variation of silicon content from 0.02 to 0.20% has also slight influence on the aimed amount of calcium. A small difference of 0.5 ppm is observed for low aluminium and low carbon content (100 ppm and 0.2%, respectively), condition in which steel tends to be in higher oxidation state. The increase of carbon content from 0.2 to 0.4% has a small impact in the calcium content, but, the impact of carbon is slightly more visible when the carbon content increases from 0.4% to 0.6%, producing an increase in the aimed calcium between 0.5 and 1 ppm. The major change in the intended calcium content occurs with the increase in sulphur content of steel. The graphs show that the increase in sulphur content in steel from 50 ppm to 150 ppm resulted in the reduction of the aimed calcium content from 15 to 13 ppm. This shows that the presence of sulphur in metallic bath expanded the formation of calcium sulphide; thus the CaS phase area increases and moves the castability window downward, i.e., to the area of lower calcium content [3,5,10].

Fig. 5 shows the “calcium range”, a term used to define the maximum gap in calcium content to obtain liquid inclusions, which corresponds to the extension of the castability window for a given condition. In practice, this variable express the difficulty to achieve the field of liquid phase inclusions after calcium treatment in the secondary refining process, especially due to great variation in the yield of the calcium cored wire. As we can see, the increase in aluminium content causes a clear reduction in the calcium range of the liquid phase. On the whole, each addition of 100 ppm in aluminium content of steel decreases about 2 ppm the calcium range. By inspecting this phenomenon, the refining process and castability of high aluminium content steel becomes much more complex than in moderate-aluminium-content steel. The main influence of silicon content occurs in conditions of low aluminium content, with greater emphasis on high carbon steel, in which the difference of calcium range varies between 3 and 4 ppm for

**Fig. 3 – Binary phase diagram aluminium vs calcium for alloy steel 0.2%C, 0.005%S, (a) 0.02%Si and (b) 0.20%Si.**

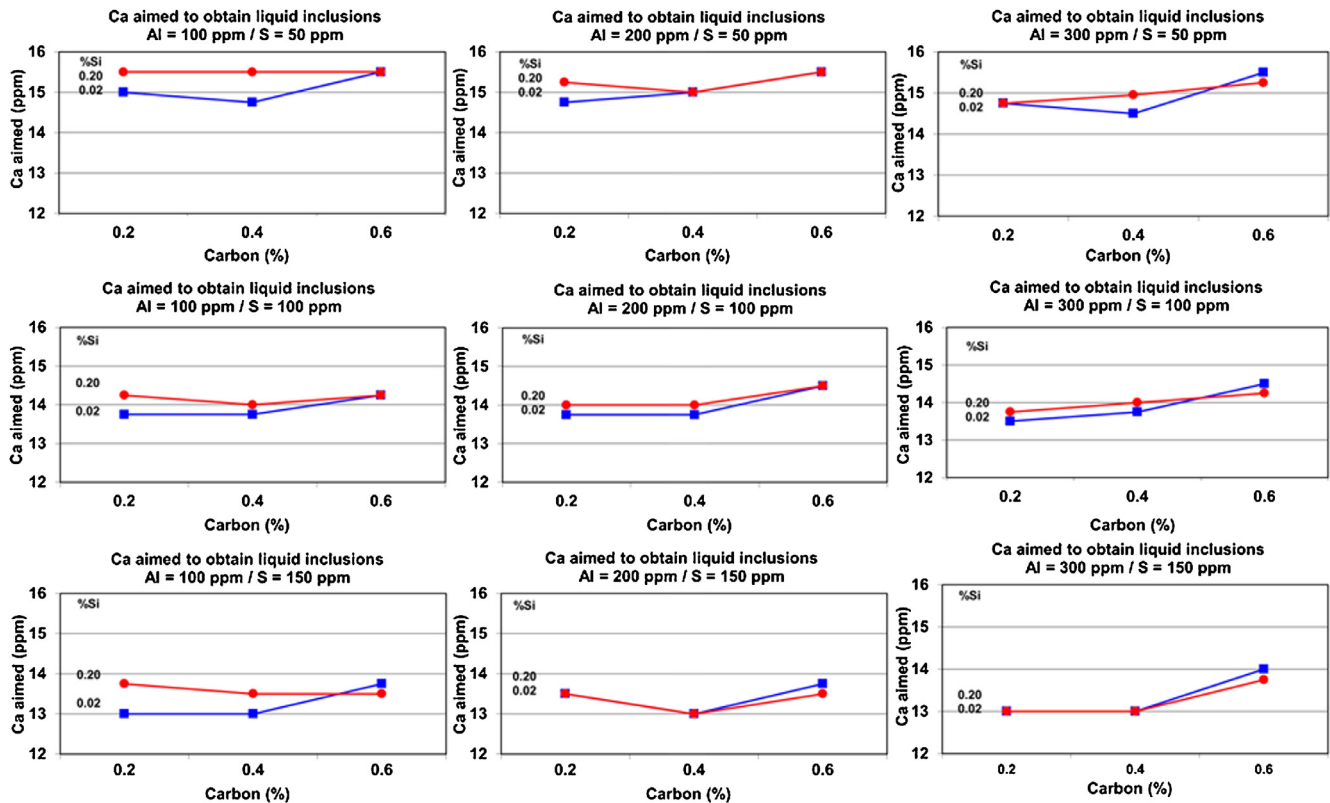


Fig. 4 – Aimed calcium content to obtain liquid inclusions. Temperature 50 °C above liquidus temperature (Table 1) and Si = 0.02 and 0.20%.

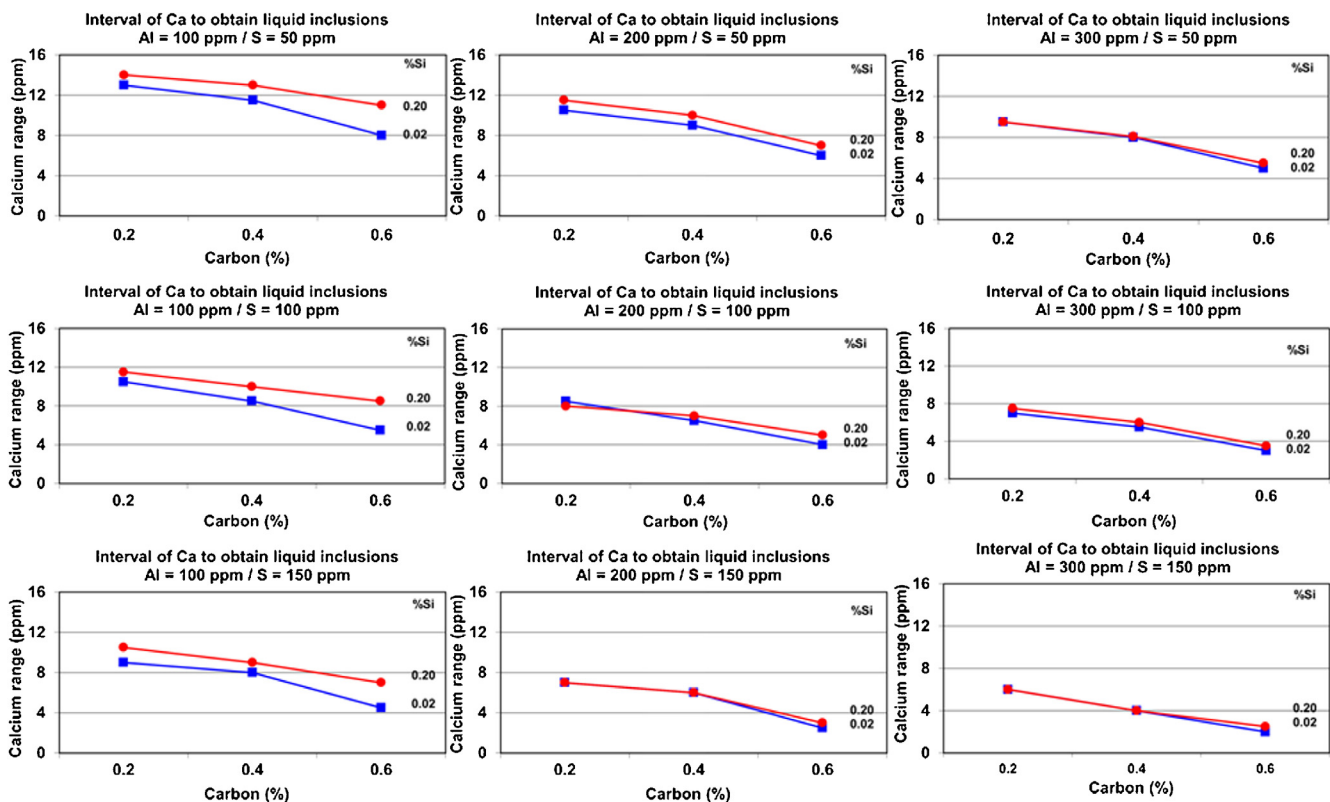


Fig. 5 – Interval in content of calcium to obtain liquid inclusions. Temperature 50 °C above liquidus temperature (Table 1) and Si = 0.02 and 0.20%.

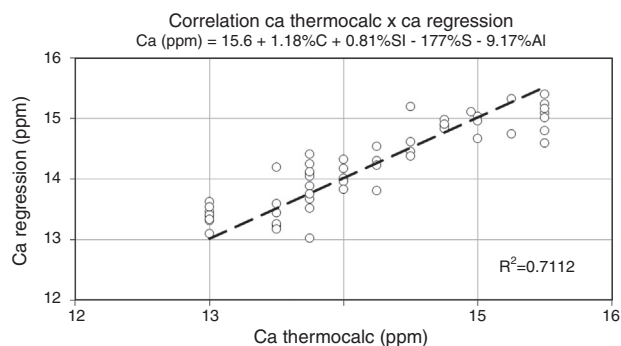


Fig. 6 – Calcium content predicted by Thermocalc vs calculated by multiple regression equation.

different silicon contents, always reduced the calcium range to 0.02% silicon content steel. Carbon content of the alloy presents clear relation with the calcium range. For all these conditions, the increase of carbon content causes an immediate reduction of the calcium range required to obtain liquid inclusions. The reduction of the calcium range is a result of a reduced castability window, and this causes an increase in the prospect of sulphides and oxides formation in solid state.

The amount of sulphur is another drawback for the formation of liquid inclusions in steel. The increase of sulphur enhances the solid inclusion area CaS and causes a flattening of the castability window. The effect of sulphur is more visible under conditions of lower steel oxidation, i.e. when percentages of carbon and aluminium are at higher level, and consequently, the total oxygen content must be lower. In the condition of S = 150 ppm, Al = 300 ppm and C = 0.4%, the gap of calcium for the adjustment of the castability window is only 4 ppm. The gap of calcium is even lower when the carbon content increases to 0.6%, a condition in which delta calcium is reduced to only 2 ppm.

A multiple linear regression was carried out using the aimed calcium data and steel chemical compositions, which matches the aimed calcium content to obtain liquid inclusions and the chemical element contents – carbon, silicon, sulphur, and aluminium. Fig. 6 shows the aimed calcium content predicted by the Thermocalc software versus those ones calculated by the multiple linear regression equation.

It is observed that the predicted and calculated data presented a good agreement, which resulted in R^2 of 89%. Although not as accurate as the software, the multiple linear

regression has an operational advantage, since the equation can be easily inserted into the metallurgical model of the melt shop and provides a fast response in the amount of calcium that should be aimed for the chemical composition fluctuations among the heats in the process.

In order to check the profile of the inclusions that solidified in the continuous casting process, it was taken a cross-sectional sample of a steel billet with 0.20%C–0.02%Si–0.01%S–0.02Al%–0.0015%Ca. The inclusions present in an area of 23 mm² of the samples were assessed through semi-quantitative analysis by SEM and is represented in the attached ternary diagram of the systems Al₂O₃–MgO–CaO and Al₂O₃–CaS–CaO (Fig. 7a).

Regarding the size, 98% of the inclusions presented diameter up to 4 μm. The first system (Al₂O₃–MgO–CaO) is to illustrate the formation of the spinel phase. This phase is formed from the combination of aluminium oxides, especially during the deoxidation of steel, and magnesium oxides, mainly by the diffusion of the magnesium ion from the refractory lining and from the slag at the ladle furnace [9]. The presence of spinel phase (Al₂O₃–MgO) and corundum (Al₂O₃) is a sign that there was no complete homogeneous transformation of calcium aluminate inclusions after calcium treatment [3]. In the Al₂O₃–CaS–CaO system, it is possible to identify the presence of CaS together with the calcium aluminates inclusions. In the studied alloy, most of the inclusions presented CaS phase in its composition. The results from the inclusions of this steel are in accordance with the newly published results for aluminium-killed low-carbon steel (Fig. 7b) [3].

The thermodynamic properties of the inclusions were calculated using the software CEQCSI. Fig. 8a shows the liquidus temperature calculated according to the full chemical composition of each inclusion.

After the calcium treatment, there are only 20% of the inclusions showing liquidus temperature below the calculated temperature of 50 °C above the steel liquidus temperature. This means that these inclusions are 100% liquid at this temperature. Another property evaluated in Fig. 8b was the amount of the liquid phase in each inclusion in the measured temperature of steel. Approximately 42% of inclusions have at least 90% of liquid phase at 50 °C above the steel liquidus temperature. In this case, the fact of having partially solid inclusions did not influence the steel flow through the nozzle at continuous caster, since the casting parameters were considered worthy. The liquidus temperature and

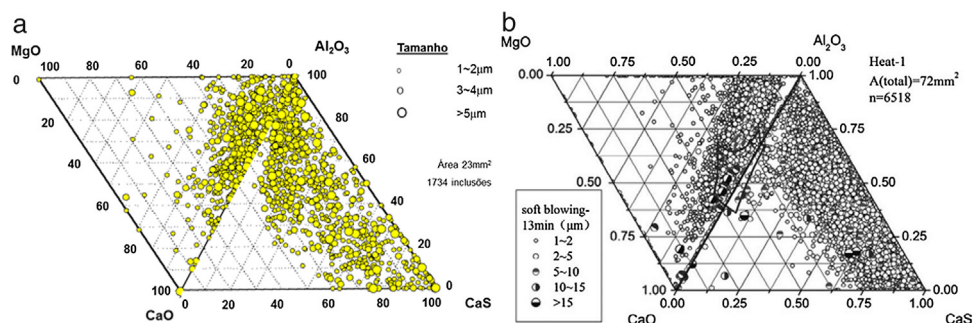


Fig. 7 – Connected ternary diagrams of the Al₂O₃–MgO–CaO and Al₂O₃–CaS–CaO systems with (a) experimental data of alloy used in this work (b) literature data [3].

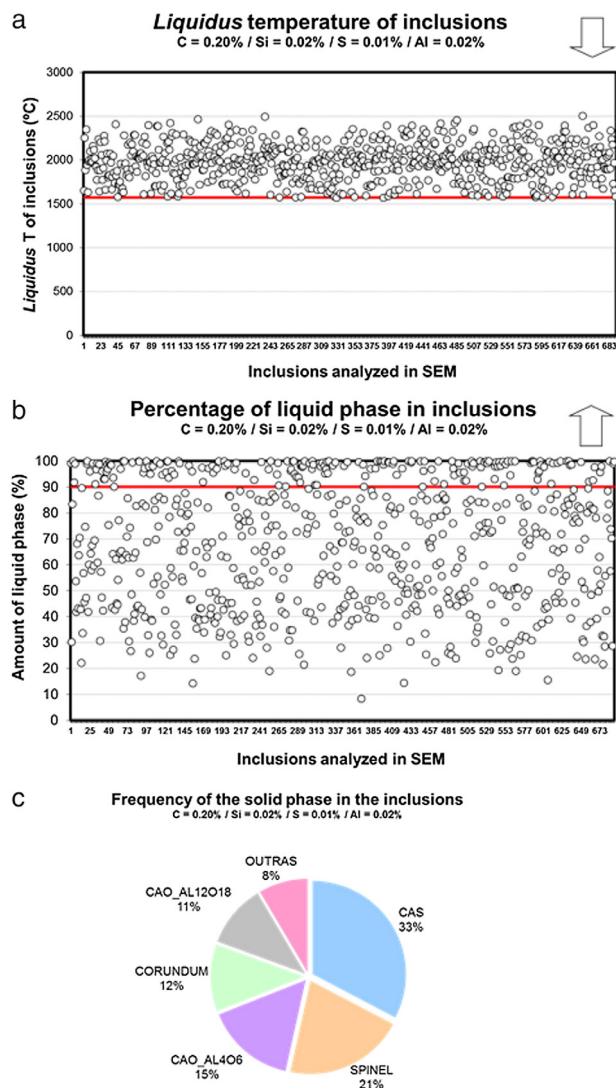


Fig. 8 – Thermodynamic properties of inclusions calculated by software CEQCSI.

the amount of the liquid phase in inclusions are important because they directly affect the steel cleanliness and castability, beyond the final properties of the product [9,10]. Fig. 8c shows the frequency of the solid phase in the inclusions found partially in solid state. Calcium sulphide (32%) is the solid inclusion of higher occurrence. The CaS is formed mainly from the relationship of additional calcium with sulphur dissolved in steel. The sulphide inclusions formed at high temperatures usually precipitate around aluminates previously formed [3]. This feature is very remarkable from the point of view of application of the product, because it benefits the spherical morphology of inclusions, which improve the results related to formation of microcracks and fatigue strength [7].

Nevertheless, the excessive CaS precipitation can damage the continuous casting process as it reduces the steel castability window, and so it must be avoided [6]. The other solid phases of higher occurrence in the inclusions are spinel, calcium aluminate and corundum. The formation of these

inclusions is a sign that their modification was unfinished. While effective, it is noted that the calcium treatment presents some degree of heterogeneity. Moreover, it is still very functional in practice, since it allows the continuous casting of long heat sequential of aluminium-killed steel and quality assurance of products manufactured by this process.

4. Conclusions

From this work, the following conclusions were achieved:

1. The aimed calcium content and the calcium range on the castability window were estimated by computer thermodynamics calculations. The amount of calcium in alloy is very important because it allows the modification of the inclusions and the sustainability of the continuous casting process.
2. Under the evaluated conditions, an increase in carbon, aluminium and sulphur contents reduces the castability window. On the other hand, an increase in silicon content expands the castability window.
3. A multiple linear regression equation with suitable correlation factor R^2 has been built, that provides a faster calculation than the thermodynamic calculation. The equation calculates the aimed calcium content in function of the aluminium, silicon, carbon and sulphur contents.
4. The ternary diagrams produced from SEM semi-quantitative analysis showed the formation of the following type of inclusions: spinel, corundum, and CaS/aluminates. The spinel and corundum phases specify a heterogeneous process of inclusions after calcium treatment.
5. The inclusions analysis of a 0.20%C–0.02%Si–/0.01%S–0.02%Al–0.0015%Ca-steel billet shows 20% of the inclusions with liquidus temperature below the casting temperature and 42% of the inclusions present over 90% of liquid phase. Regardless of heterogeneous characteristics, the calcium treatment allows continuous casting of aluminium-killed steel.

Conflicts of interest

The authors declare no conflicts of interest.

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REFERENCES

- [1] Van Ende MA, Guo M, Zinngrube E, Blanpain B, Jung JJ. Evolution of non-metallic inclusions in secondary steelmaking: learning from inclusion size distributions. *ISIJ Int* 2013;53(11):1974–82.
- [2] Choudhary SK, Chandra S. Castability of Mn–Si killed low carbon wire rod steel. *ISIJ Int* 2007;47(1):190–2.

- [3] Yang W, Zhang L, Wang X, Ren Y, Liu X, Shan Q. Characteristics of inclusions in low carbon Al-killed steel during ladle furnace refining and calcium treatment. *ISIJ Int* 2013;53(8):1401–10.
- [4] Costa e Silva AV. Aplicações da termodinâmica computacional aplicada a aciaria. In: *Proceedings of the XXXVII Seminário de Aciaria Internacional da ABM*. Brazilian Association of Metallurgy, Organizer; 2006, May.
- [5] Magalhães H [master thesis] Melhoria da limpidez do aço SAE 1045 desoxidado ao alumínio com aplicação na indústria automobilística, utilizando termodinâmica computacional. Ouro Preto, Brazil: REDEMAT/UFOP; 2010, February.
- [6] Costa Neto JG, Lino RE, Marins AMF, Marchi LA, Ferreira HC. Termodinâmica computacional: aplicações práticas na fabricação do aço. In: *Proceedings of the 67 Congresso da ABM Internacional*. Rio de Janeiro, Brazil: Brazilian Association of Metallurgy, Organizer; 2012.
- [7] Jiang M, Wang X, Chen B, Wang W. Laboratory study on evolution mechanisms of non-metallic inclusions in high strength alloyed steel refined by high basicity slag. *ISIJ Int* 2010;50(1):95–104.
- [8] Turkdogan ET. *Fundamentals of Steelmaking*. London: The Institute of Materials; 1996 [Chapter 9].
- [9] Park JH, Todoroki H. Control of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel inclusions in stainless steels. *ISIJ Int* 2010;50(10):1333–46.
- [10] Choudhary SK, Ghosh A. Thermodynamic evaluation of formation of oxide–sulfide duplex inclusions in steel. *ISIJ Int* 2008;48(11):1552–9.
- [11] Lino RE, Marins AMF, Penna LV, Costa Neto JG, Caldeira JHP, Costa e Silva AV. Determinação de temperatura liquidus de aços. In: *Proceedings of the 68 Congresso da ABM Internacional*. Belo Horizonte, Brazil: Brazilian Association of Metallurgy, Organizer; 2013.